Oxidative removal of 4-nitrophenol using activated carbon fiber and hydrogen peroxide to enhance reactivity of metallophthalocyanine

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ARTICLE INFO

ABSTRACT

We have developed a novel heterogeneous metallophthalocyanine catalyst, Co-TDTAPc–ACF, by immobilizing cobalt tetra(2,4-dichloro-1,3,5-triazine)aminophthalocyanine (Co-TDTAPc) on activated carbon fiber (ACF) covalently. The oxidative removal of 4-nitrophenol (4-NP) in the Co-TDTAPc–ACF/ H_2O_2 system, based on phase transfer catalytic oxidation, was investigated in aqueous solution by ultra-performance liquid chromatography (UPLC). The results indicated that 4-NP could be removed efficiently by catalytic oxidation in the presence of Co-TDTAPc–ACF and H_2O_2. In addition, the removal of total organic carbon of 4-NP accounted for about 90% in 300 min of reaction. Gas chromatography/mass spectrometry (GC–MS) analysis showed that the residue products were mainly small molecular compounds such as maleic acid and succinic acid, etc. This system exhibited high catalytic activity across a wide pH and temperature range. Importantly, compared with homogeneous Co-TDTAPc used alone, the introduction of ACF contributed specifically to the activity enhancement of Co-TDTAPc. Controlled experiments showed that the presence of 2-propanol, as hydroxyl radicals scavenger, has little influence on 4-NP oxidation. The further result of electron paramagnetic resonance (EPR) spin-trap experiments indicated that free radicals did not dominate the reaction in our system. This paper discusses a possible catalytic oxidation mechanism of the Co-TDTAPc–ACF/H_2O_2 system. Repetitive tests showed that Co-TDTAPc–ACF can maintain high catalytic activity over several cycles, and it has a better regeneration capability under mild conditions. We conclude that phase transfer catalytic oxidation has proven itself to be a feasible approach which may be potentially applied to the elimination of widely existing pollutants.

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1. Introduction

Organic compounds are widely dispersed and likely to occur as environmental hazards in water. Among different organic pollutants, phenols have been designated as priority pollutants by many countries due to their acute toxicity and long persistence [1]. Thus, they must be degraded to below environmentally accepted levels before safe disposal to public health. Various technologies, such as biodegradation [2,3], adsorption [4–9], catalytic wet oxidation [10–13], advanced oxidation processes (AOPs), etc., have been conventionally used for phenols treatment. Because phenols are harmful to organisms, disrupting energy conversion processes in cellular and subcellular membranes even at low concentrations, biological treatments have a limited capacity for degrading them, especially when the phenols are at high concentrations [14–16]. Activated carbons, the most common adsorbent, have been used to treat phenols, but limited by their difficult regeneration. A number of regeneration processes of activated carbons have been reported. However, thermal regeneration is expensive and may result in fraction of the carbon losing, and chemical regeneration usually introduces extra reagents [17–23].

AOPs (e.g., H_2O_2/UV, O_3/UV, O_3/H_2O_2, Fenton's reagent, photo-Fenton, photocatalysis, electrochemical oxidation, etc.) have been applied to remove phenols effectively [24–32], while some oxidation processes need energy light sources, like ultraviolet light, and may bring secondary pollution. To overcome secondary pollution, supported catalyst systems have been also proposed. But the supports may negatively affect catalyst utilization, especially in photocatalysis systems, where some of the active sites are hidden inside the support and not accessible by the light [33]. Therefore, there is a clear need for more efficient and feasible approaches to removing phenols from wastewater, where the activity of catalysts can be maintained or improved and secondary pollution may be controlled.

The advantageous and eco-friendly procedures emphasize that water treatment technologies are more effective against pollutants in reducing energy consumption under mild conditions. Moreover, the final products of these technologies do not harm the

environment and can be biodegraded further. In light of the above considerations, we recently demonstrated that a new method, "phase transfer in situ catalytic oxidation," which is based on cellulosic fiber supported metallophthalocyanines, can be applied to eliminate various dyes [34], but this system proved less efficient for the removal of phenols, probably due to the low adsorption of phenols onto cellulosic fibers or to the relatively low catalytic activity. In order to solve these problems, we hypothesized that using better materials to support the metallophthalocyanines would enable the efficient oxidative removal of phenols.

Activated carbon fiber (ACF) has extremely high adsorption capacity and unusual chemical stability. Hence, it has been intensively used to remove organic pollutants, including various phenols [35–39]. Because of its remarkable properties, we chose ACF as the support for the metallophthalocyanines in our phase transfer catalytic oxidation system. We immobilized cobalt tetra(2,4-dichloro-1,3,5-triazine)aminophthalocyanine (Co-TDTAPc) covalently on ACF to obtain a novel heterogeneous catalyst, and constructed a phase transfer catalytic oxidation system: Co-TDTAPc–ACF/H_2O_2. This article presents the results of our investigation of the catalytic oxidation processes of 4-nitrophenol (4-NP) as models, using ultra-performance liquid chromatography (UPLC) and gas chromatography/mass spectrometry (GC–MS). Electron paramagnetic resonance (EPR) spin-trap technique was employed to probe the possible mechanism in our system. We also report on our tests of the key influencing factors (e.g., pH and temperature) and discuss the whole catalytic oxidation process.

2. Experimental

2.1. Materials and reagents

ACF was obtained from Jiangsu Sutong Carbon Fiber Co., Ltd. (Jiangsu, China). Cobalt chloride hexahydrate, urea, ammonium molybdate, cyanuric chloride, and hydrogen peroxide (9.7 M, Sinopharm Chemical Reagent Co., Ltd.) were used as analytical reagents. Trimethylsulfonium hydroxide and the spin trapping reagent 5,5-dimethyl-pyrroline-oxide (DMPO) was supplied by Tokyo Chemical Industry Co., Ltd. 4-NP was of laboratory reagent grade and was used without further purification. Doubly distilled water was used throughout the 4-NP removal experiments. All other solvents were of spectrometric grade.

2.2. Preparation of Co-TDTAPc–ACF

Co-TDTAPc was synthesized from cobalt tetraaminophthalocyanine and cyanuric chloride according to the method described by Chen et al. [34]. ACF has experienced acidizing, water washing and drying. Co-TDTAPc–ACF was prepared by immobilizing Co-TDTAPc to acidulated ACF by bonding it covalently (see Supplementary Information for details of the process).

2.3. Oxidation procedures and analysis

The catalytic oxidation of 4-NP was carried out in a 250 mL glass beaker. The temperature was controlled at 25 °C or other temperature by a constant temperature shaker water bath (DSHZ-300A, Taicang Laboratorial Equipment Factory, China). A typical reaction mixture contained the following concentrations or initial amounts: 4-NP (0.5 mM), Co-TDTAPc–ACF (2 g/L, containing 33 μM cobalt phthalocyanine (CoPc)), ACF (2 g/L), Co-TDTAPc (33 μM) and H_2O_2 (100 mM). The aqueous solution was adjusted to different pH values by a diluted aqueous solution of NaOH or $HClO_4$. The reactions were allowed to proceed for various amounts

of time and then quenched by a method appropriate to the analysis. At given time intervals, the samples were analyzed immediately by UPLC (waters) equipped with the Acquity UPLC BEH C18 column (1.7 μm, 2.1 mm × 50 mm). The binary system phases were (A) water with 0.1% H_3PO_4 and (B) acetonitrile; the eluent was A and B (1:1, v/v) with a flow rate of 0.4 mL min^{-1}. Detection was accomplished using a photodiode array detector set at 317 nm for 4-NP. TOC analysis for 4-NP solution was performed using a Shimadzu TOC-VCPH analyzer. For analysis of the residual organics from 4-NP oxidation, after reaction for 300 min, the reaction solution in the presence of Co-TDTAPc–ACF and H_2O_2 was withdrawn. Samples for GC–MS analysis were prepared by methyl esterification with trimethylsulfonium hydroxide (see Supplementary Information). Electron paramagnetic resonance (EPR) signals of radicals trapped by DMPO were recorded at ambient temperature on a Brucker E500 spectrometer. The settings for the EPR spectrometer were the following: center field, 3480 G; sweep width, 100 G; microwave frequency, 9.77 GHz; modulation frequency, 100 kHz; power, 12.72 mW.

3. Results and discussion

3.1. Oxidative removal of 4-NP

With the aim of investigating the catalytic activity of Co-TDTAPc–ACF, we selected 4-NP in aqueous solution as the substrate for the catalytic oxidation. As shown in Fig. 1, 4-NP did not disappear in the presence of H_2O_2 without any catalyst. However, 4-NP decreased by 67% using Co-TDTAPc–ACF alone for 300 min, which was attributed to the good adsorption capacity of ACF, while the adsorption process reached basically equilibrium. When 4-NP in aqueous solution was exposed to Co-TDTAPc–ACF and H_2O_2 together, the catalyst removed more than 97% of the 4-NP. Moreover, experiments indicated that such a result could not be obtained in the presence of Co-TDTAPc and H_2O_2, where the molar content of CoPc in the Co-TDTAPc was the same as that in the Co-TDTAPc–ACF/H_2O_2 system. The results of these investigations demonstrate that the catalytic performance of Co-TDTAPc–ACF is superior to that of homogeneous Co-TDTAPc. In addition, the presence of H_2O_2 does not accelerate the adsorption of 4-NP on ACF
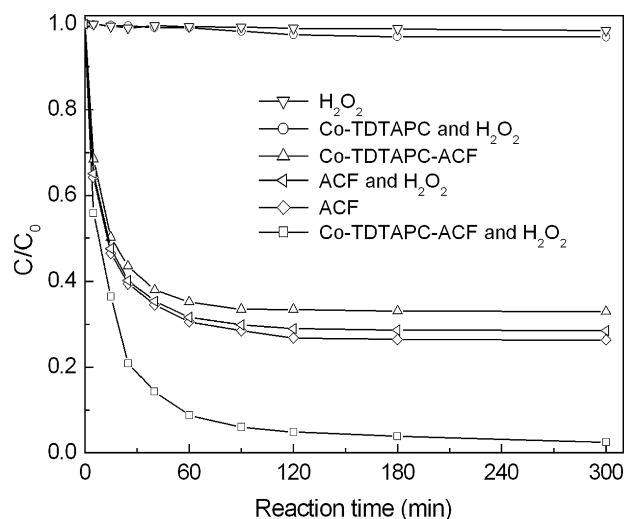

Fig. 1. Concentration changes of 4-NP (0.5 mM) under different conditions (pH 6.84, T = 25 °C): (a) H_2O_2 (100 mM); (b) Co-TDTAPc (33 μM) and H_2O_2 (100 mM); (c) Co-TDTAPc–ACF (2 g/L, containing 33 μM CoPc); (d) ACF (2 g/L) and H_2O_2 (100 mM); (e) ACF (2 g/L); (f) Co-TDTAPc–ACF (2 g/L, containing 33 μM CoPc) and H_2O_2 (100 mM).

and there is little catalytic role of ACF on the oxidation of 4-NP in the presence of H_2O_2. The immobilized CoPc slightly decreases the total number of adsorption sites of ACF. But this catalyst can maintain good adsorption ability for the transfer catalytic oxidation of 4-NP in the presence of H_2O_2. Hence, we can consider that the introduction of ACF into our system enhanced the reactivity of Co-TDTAPc with H_2O_2. In some catalytic systems, studies have reported improving the catalytic performance of a catalytic entity by supporting it using other materials [40–43]. In our study, the removal of TOC of 4-NP accounted for about 90% in 300 min of reaction. This indicates that a substantial amount of 4-NP was converted to other organic products, besides a small quantity of residual 4-NP. GC–MS analysis demonstrated that most of the 4-NP was oxidized into less-toxic and more-biodegradable compounds, such as maleic acid and succinic acid, etc., after catalytic oxidation for 300 min (See Supplementary Information).

In order to investigate the sustaining catalytic ability of Co-TDTAPc–ACF, several oxidation processes to catalyze 4-NP were carried out sequentially by adding the same amount of 4-NP, with or without H_2O_2, every 300 min. As can be seen in Fig. 2, the amount of residual 4-NP in aqueous solution increased remarkably by adding 4-NP without H_2O_2 and finally reached 1.34 mM. However, when we repeated the above experiment with H_2O_2, the remaining 4-NP concentration was only 0.11 mM. This suggests that the adsorbed 4-NP in the Co-TDTAPc–ACF system was oxidized and that 4-NP in solution can enter into Co-TDTAPc–ACF, resulting in the tremendous decrease of 4-NP in solution. Our results support the view that this phase transfer catalyst, Co-TDTAPc–ACF, can be reused and recovered for the catalytic oxidation of 4-NP without obvious decrease of catalytic activity.

3.2. Regeneration of Co-TDTAPc–ACF

It seems very important to consider whether catalytic oxidation could still take place effectively after the adsorption of 4-NP to Co-TDTAPc–ACF reached equilibrium. As shown in Fig. 3, in the presence of Co-TDTAPc–ACF alone, the removal rate of 4-NP was about 66% in 180 min. Almost no change occurred during the next 180 min, which indicates that the adsorption of 4-NP was close to saturation by the end of the initial 180 min. After adding H_2O_2 to the adsorption equilibrium system, the concentration of 4-NP in
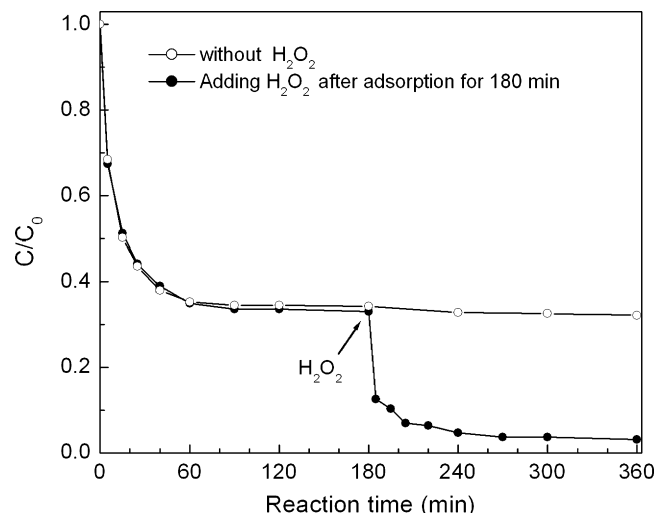

Fig. 3. Concentration changes of 4-NP (0.5 mM) after adsorption with (100 mM) or without H_2O_2 (pH 6.84, $T = 25$ °C).

solution reduced dramatically, implying that the 4-NP adsorbed onto Co-TDTAPc–ACF system was oxidized rapidly; thus this implies that 4-NP in solution can be quickly enriched. Above experiments (Fig. 1) indicated that the presence of H_2O_2 does not accelerate the adsorption of 4-NP on ACF. Therefore, the results suggest that the catalytic oxidation of 4-NP proceeds rapidly. The adsorption of 4-NP to Co-TDTAPc–ACF enables the anchoring of 4-NP near the active sites, realizing rapid and effective catalytic oxidation within a noticeably short time. On the basis of the analysis above, it may confirm that Co-TDTAPc–ACF has a possibility of self-reliance regeneration in this phase transfer catalytic oxidation system.

Since the catalytic oxidation of 4-NP in the Co-TDTAPc–ACF/H_2O_2 system includes two processes, adsorption and oxidation, to investigate the regeneration performance, we designed a period-ical experiment. When the adsorption of 4-NP in solution onto Co-TDTAPc–ACF reached equilibrium without H_2O_2, the saturated catalyst was immersed into an aqueous solution with H_2O_2 for 180 min of catalytic oxidation. The catalyst was taken out, rinsed with deionized water to remove H_2O_2, and dried in vacuum at room temperature. This process was repeated five more times. As shown in Fig. 4, the adsorption removal of 4-NP after 120 min was about 66% by the end of the first cycle. After repeating this experiment six times, it was as high as 63% and had no obvious decrease, suggesting that most 4-NP adsorbed onto the Co-TDTAPc–ACF was oxidized in the presence of H_2O_2, and otherwise their residues would influence subsequent adsorption process. Therefore, not only can Co-TDTAPc–ACF realize enrichment and simultaneous catalytic oxidation, but it also retains a better ability to regenerate on-site. Importantly, compared with common thermal regeneration, no external energy is involved in regenerating Co-TDTAPc–ACF; since this is an oxidation regeneration process, it represents a "real" removal of the substrate, not simply its transfer from solution to adsorbent or from adsorbent to another environment.

3.3. Effect of pH and temperature

Wastewater from industry usually has a certain range of pH values, while some treatment methods are pH dependent [44,45]. Accordingly, an attempt was made to study the influence of pH on the oxidative removal of 4-NP at pH values in the range of 3.15–11.12; the removal rates of 4-NP after 300 min using Co-TDTAPc–
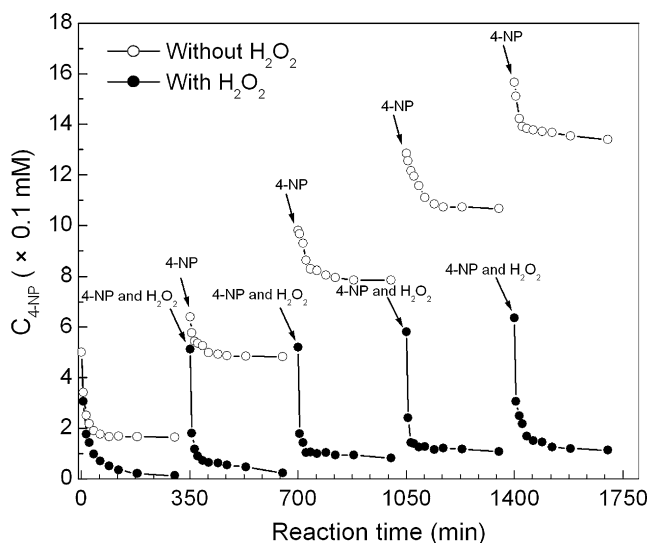

Fig. 2. Concentration changes of 4-NP (initial concentration: 0.5 mM) with continuous addition of 4-NP with H_2O_2 (initial concentration: 100 mM) or without H_2O_2 (pH 6.84, $T = 25$ °C). The four subsequent identical additions of 4-NP resulted finally in 2.5 mM 4-NP and 500 mM H_2O_2.
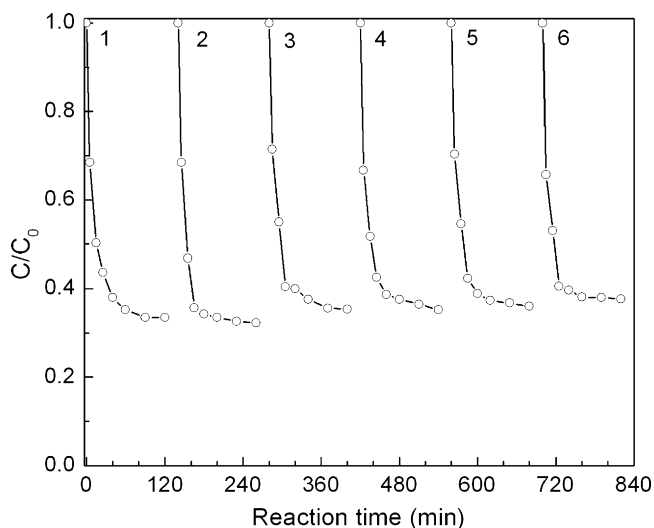
Fig. 4. Concentration changes of 4-NP (0.5 mM) in aqueous solution without H_2O_2 in repetitive adsorption process after oxidative regeneration in aqueous solution with H_2O_2 (100 mM) (pH 6.84, T = 25 °C).
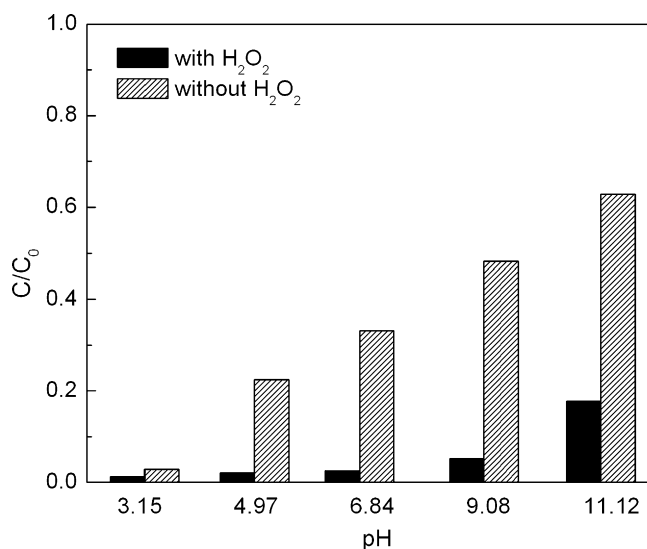

Fig. 6. Effect of temperature on adsorption and catalytic oxidation of 4-NP (0.5 mM) in the presence of Co-TDTAPc–ACF (2 g/L) with H_2O_2 (100 mM) or without H_2O_2 (pH 6.84).

metallophthalocynine, the Co-TDTAPc–ACF/H_2O_2 system efficiently eliminated phenolic compounds in neutral aqueous solutions. Therefore, our results confirm that this phase-transfer catalytic oxidation system is more advantageous than either the homogeneous or heterogeneous Fenton systems, where catalytic oxidation mostly takes place in acid solutions [46]. In addition, our covalently supported metal complex catalytic system can overcome the loss of catalyst in some heterogeneous metal and metal oxide at low pH, just like iron and iron oxides.

We also investigated the effect of temperature on the rate of 4-NP removal in another set of experiments. As Fig. 6 shows, the adsorption of 4-NP to Co-TDTAPc–ACF after 300 min in the absence of H_2O_2 decreased with the increase of temperature, since adsorption to common activated carbon materials belongs to a spontaneous and exothermic process, in accordance with the experimental results in some studies on the adsorption process of activated carbon [36,47]. However, in the presence of H_2O_2, Co-TDTAPc–ACF was able to catalyze the oxidative removal of 4-NP efficiently over a wide range of temperatures, though the 4-NP removal rates decreased slightly as temperature increased. We believe that the high adsorption capability of Co-TDTAPc–ACF could positively affect the oxidative removal of 4-NP and enable proceeding at relatively low temperatures. This approach provides a simple idea for improving common catalytic oxidation systems, where the catalytic efficiency decreases as the reaction temperature descends.

3.4. Analysis of the catalytic oxidation process and mechanism

The results presented in this paper demonstrate that, due to its outstanding adsorption capability, Co-TDTAPc–ACF can rapidly transfer 4-NP from an aqueous solution to the micropores in ACF. In the presence of H_2O_2, the catalytic oxidation of 4-NP occurs immediately, and 4-NP in an aqueous solution can be enriched continuously into Co-TDTAPc–ACF until its removal is complete. During the entire process of oxidatively removing 4-NP, adsorption and catalytic oxidation facilitate one another, accelerating the catalytic oxidation process and achieving on-site regeneration. This might be attributed to the fact that ACF provides a predominant enrichment of catalytic active sites and improves catalytic oxidation efficiency by concentrating substrates from

Fig. 5. Effect of initial pH on adsorption and catalytic oxidation of 4-NP (0.5 mM) in the presence of Co-TDTAPc–ACF (2 g/L) with H_2O_2 (100 mM) or without H_2O_2 (T = 25 °C).

ACF and Co-TDTAPc–ACF/H_2O_2 are shown in Fig. 5. Without H_2O_2, the removal rates were 97.4%, 66.5% and 37.2% at pH values of 3.15, 6.84 and 11.12, respectively, indicating that the adsorption capability of Co-TDTAPc–ACF to 4-NP decreased with the increase of pH. At the same pH values, the Co-TDTAPc–ACF/H_2O_2 system achieved 4-NP removal rates of 99.9%, 97.1% and 82.3%, showing a small, gradual increase in the amount of 4-NP existing in solution with the increase of pH. These phenomena can be explained by means of the dissociation of 4-NP. In acid conditions, the adsorption of 4-NP from aqueous phase to Co-TDTAPc–ACF occurred very rapidly. As pH increased, more and more of the soluble 4-NP was in its dissociated form [45], which reduced the adsorption of 4-NP because of the dominant electrostatic repulsion between the dissociated 4-NP and electronegative oxygen-containing functional groups. Since the oxidative removal of 4-NP occurred rapidly, this system proved itself able to reach higher catalytic efficiency in acid, neutral, and basic conditions. Compared with our previous study of the use of cellulose to support
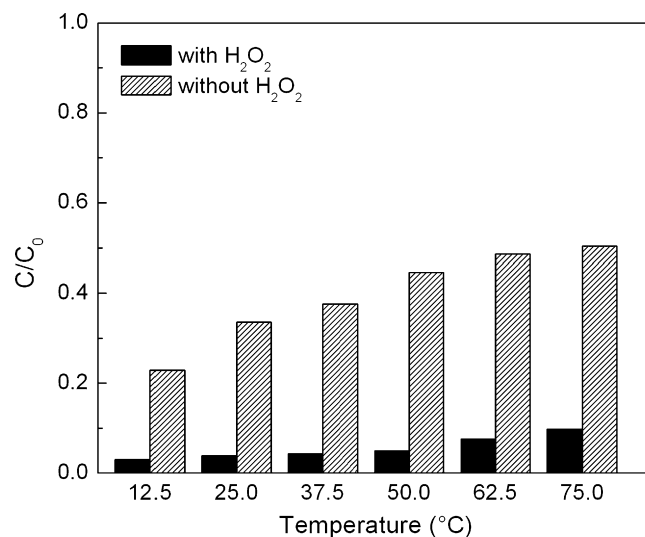
solution dozens, and even hundreds, of times. Thus, the clearly enhanced activity of Co-TDTAPc is most likely due to the introduction of ACF.

The oxidation mechanisms of organic pollutants with H_2O_2 catalyzed by iron[III] phthalocyanine has been studied, including the following two kinds of mechanisms with different reactive species: free hydroxyl radicals [48,49] and iron-peroxo complex PcSFeOOH [24,50,51]. But little has been reported on the catalytic oxidation mechanism of CoPc with H_2O_2 as the oxidant. In order to gain a deeper insight into the reaction mechanism, 2-propanol, a typical hydroxyl radicals scavenger [52], was used to investigate the catalytic performance of Co-TDTAPc–ACF. As shown in Fig. 7, in the presence of 2-propanol, Co-TDTAPc–ACF gave 66.9% adsorption of 4-NP after 300 min, while the Co-TDTAPc–ACF/H_2O_2 system gave 96.5% removal—results that were nearly equivalent to those in the absence of 2-propanol (Fig. 1). This implies that the catalytic oxidation of 4-NP in 2-propanol is unlikely to involve predominant free hydroxyl radicals, because the introduction of 2-propanol could lead to an obvious decrease of catalytic activity in the system based on free hydroxyl radicals [52,53].

To further investigate the role of ACF in Co-TDTAPc–ACF/H_2O_2, we introduced a copolymer of cobalt tetra(N-carbonylacrylic)a-minophthalocyanine and N-isopropylacrylamide (CoPc-NIPA) as a homogeneous catalyst, which has a similar catalytic activity to Co-TDTAPc in aqueous solution, but has good solubility in some alcoholic solvents. The EPR spin-trap technique (with DMPO) was employed to probe the possible reactive oxygen species. As shown in Fig. 8, no DMPO-OH signals were detected in both Co-TDTAPc–ACF/H_2O_2 and CoPc-NIPA/H_2O_2 systems, which means that hydroxyl radical is not the major intermediate of the CoPc-catalyzed H_2O_2 reaction. In 2-propanol solvent (Fig. 9), the DMPO-OOH species were detected in CoPc-NIPA/H_2O_2 system (Fig. 9a), which reveals that OOH plays a key role in this homogeneous CoPc catalytic system. However, no DMPO-OOH species were observed in Co-TDTAPc–ACF/H_2O_2 system (Fig. 9b), suggesting that ACF result in a different reaction pathway from free radicals pathway to non-radical mechanism, and open up a new channel to specifically enhance the CoPc activity. The interconnected mesopores and ultramicropores in ACF show rapid charge propagation and accumulation [37,39] and this system can generate some local high electric potential sites, sequentially accelerating the oxidative removal of 4-NP. In addition, the electrical conductivity of ACF can also assist the electron transfer reactions among H_2O_2, Co-TDTAPc–ACF, and 4-NP. The control experiment indicated that
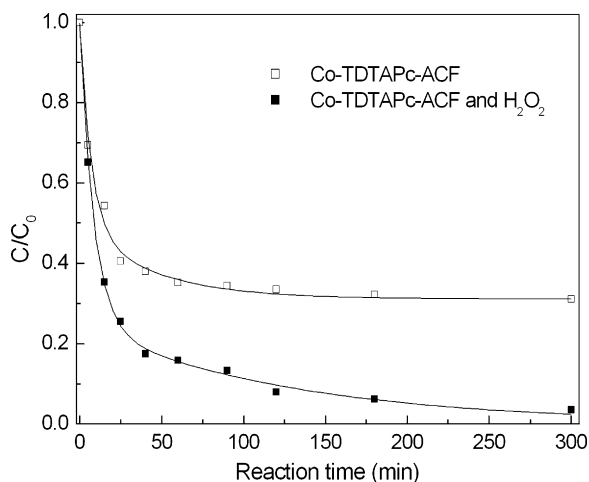

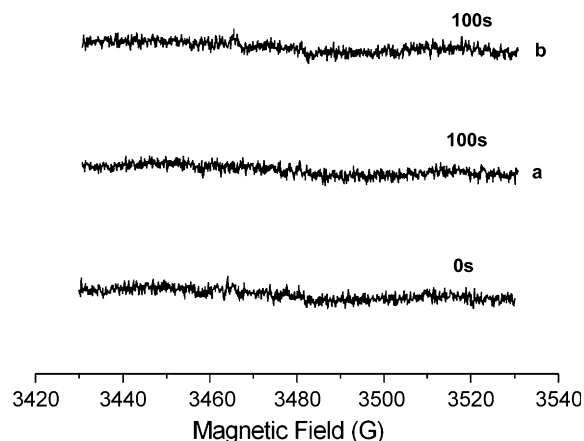**Fig. 8.** DMPO spin-trapping EPR spectra in 4-NP (0.5 mM) aqueous solutions in the presence of (a) Co-TDTAPc–ACF (2 g/L, containing 33 μM CoPc) or (b) CoPc-NIPA (3.54 g/L, containing 33 μM CoPc) with H_2O_2 (100 mM) and DMPO (20 mM).

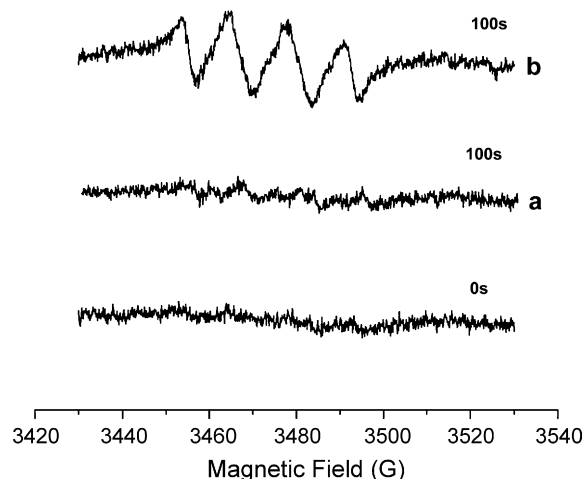**Fig. 9.** DMPO spin-trapping EPR spectra in 4-NP (0.5 mM) 2-propanol solutions in the presence of (a) Co-TDTAPc–ACF (2 g/L, containing 33 μM CoPc) or (b) CoPc-NIPA (3.54 g/L, containing 33 μM CoPc) with H_2O_2 (100 mM) and DMPO (20 mM).

homogeneous CoPc-NIPA catalyst has no activity on the oxidation of 4-NP in neutral aqueous solution with H_2O_2. It is therefore obvious that the introduction of ACF can change the catalytic pathway and enhance the catalytic activity of CoPc by a different electron transfer channel.

4. Conclusions

The novel and highly efficient catalytic oxidation system of Co-TDTAPc–ACF/H_2O_2 offers a promising method for the rapid removal of 4-NP. The system's simultaneous processes of adsorption and catalytic oxidation allow the spontaneous regeneration of Co-TDTAPc–ACF. The introduction of ACF significantly enhanced the rate of catalytic oxidation of 4-NP based on a new catalytic pathway, and resulted in a novel catalytic performance that analogous homogeneous CoPc catalysts did not exhibit. Furthermore, as an improved phase transfer catalytic oxidation system, Co-TDTAPc–ACF/H_2O_2 may be identified as a potential conventional approach to treat wastewater by combining enrichment and catalytic oxidation together. Depend on the self-reliance regeneration capability of Co-TDTAPc–ACF in the presence of H_2O_2, it is expected to provide a technology capable of being operated in a continuous and efficient mode to treat organic pollutants.

Fig. 7. Concentration changes of 4-NP (0.5 mM) in the presence of Co-TDTAPc–ACF (2 g/L) in 2-propanol (13.06 mM) with H_2O_2 (100 mM) or without H_2O_2 (T = 25 °C).

Acknowledgements

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.apcatb.2008.08.024.

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